

Aging phenomena in polystyrene thin films

K. Fukao¹ and H. Koizumi¹

¹ *Department of Polymer Science, Kyoto Institute of Technology, Matsugasaki,
 Kyoto 606-8585, Japan*

Abstract

The aging behavior is investigated for thin films of atactic polystyrene through measurements of complex electric capacitance. During isothermal aging process the real part of the electric capacitance increases with aging time, while the imaginary part decreases with aging time. This result suggests that the aging time dependence of the real and imaginary parts are mainly associated with change in thickness and dielectric permittivity, respectively. In thin films, the thickness depends on thermal history of aging even above the glass transition. Memory and ‘rejuvenation’ effects are also observed in the thin films.

1 INTRODUCTION

Polymeric glasses show structural changes during aging process below glass transition temperature T_g , and corresponding changes in many physical quantities are observed [1,2]. These phenomena known as physical aging are regarded as an important common property characteristic of disordered materials including polymer glasses [3–5] and spin glasses [6,7]. In our previous papers [4,5], it is found for thin films of poly(methyl methacrylate) (PMMA) that the dielectric constant decreases with aging time during aging process, and that the thin films show memory and rejuvenation that depend on thickness.

The glass transition dynamics of thin films of atactic polystyrene (a-PS) have been investigated most intensively, and it has been reported that the glass transition temperature T_g is drastically decreased and the dynamics of the α -process becomes faster with decreasing film thickness [8–12]. Therefore, it should be an interesting question whether the aging dynamics below T_g can also be affected by the decrease in T_g in thin film geometry. In this paper, we investigate the aging phenomena for thin films of a-PS through measurements of complex electric capacitance.

2 EXPERIMENT

Thin films of atactic polystyrene (a-PS) with the thickness d of 14 nm and 293 nm (bulk) were prepared using a spin-coat method from a toluene solution of a-PS on Al-deposited glass substrate. The samples of a-PS used in this study were purchased from Aldrich Co., Ltd. ($M_w=1.8 \times 10^6$, $M_w/M_n = 1.03$). The preparation methods for thin films are the same as in our previous papers [9,10]. The values of T_g in thin films with $d=14\text{nm}$ and 293nm are 350 K and 370 K, respectively.

Capacitance measurements were done using an LCR meter (HP4284A) for the frequency f from 20 Hz to 1MHz during the cooling and heating processes between 380K and 273K at a rate of 1K/min and also during isothermal aging at various aging temperatures T_a ($=321.3 \text{ K} \sim 305.8\text{K}$). In our measurements, the complex electric capacitance of the sample condenser $C^*(\equiv C' - iC'')$ was measured as a function of temperature T and aging time t . The value of C^* can be converted into the dynamic (complex) dielectric constant $\epsilon^*(\equiv \epsilon' - i\epsilon'')$ by dividing the $C^*(T)$ by the geometrical capacitance $C_0(T_0)$ at a standard temperature T_0 . The value of C^* is given by $C^* = \epsilon^* \epsilon_0 \frac{S}{d}$ and $C_0 = \epsilon_0 \frac{S}{d}$, where ϵ_0 is the permittivity in vacuum, S is the area of the electrode. For evaluation of ϵ^* and C_0 , we use the thickness d which is determined at $T_0=293 \text{ K}$ and $S=8 \text{ mm}^2$.

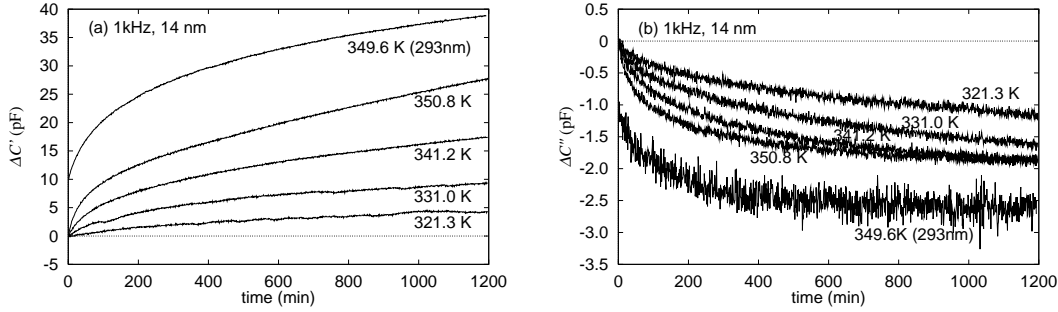


Fig. 1. Aging time dependence of the deviation $\Delta C'(t)$ ($\Delta C''(t)$) of $C'(t)$ ($C''(t)$) from the initial values $C'(0)$ ($C''(0)$) for various aging temperatures for thin films of a-PS with film thickness of 14nm for $f=1\text{kHz}$. The aging temperatures T_a are 350.8K, 341.2K, 331.0K and 321.3K. As a reference, the results for $d=293\text{nm}$ are also shown after rescaling and shifting along the vertical axis.

3 AGING DYNAMICS

Fig.1 shows aging time dependence of C' and C'' during the isothermal aging for $d=14\text{nm}$ at various values of T_a . In Fig.1(a), the deviation $\Delta C'$ of C' from the value at the initial time, at which the temperature of the sample reaches the aging temperature, increases monotonically with aging time and the amount of the relaxation for the isothermal aging at T_a for 20 hours decreases with decreasing T_a . In Fig.1(b), on the other hand, it is found that $\Delta C''$ decreases with increasing aging time and the amount of the relaxation of C'' decreases with decreasing T_a . Comparing the results observed for $d=293\text{nm}$ with those for $d=14\text{nm}$, it is found that the time dependence of $\Delta C'$ ($\Delta C''$) for $d=14\text{nm}$ is similar to that for $d=293\text{nm}$, the relaxation strength depends on film thickness. As for the frequency dependence, we could observed that as f increases, $\Delta C''$ decreases, while $\Delta C'$ remains almost constant. The detailed dependence on d and f will be reported elsewhere.

Here, an explanation for the observed dependence of C' and C'' on the aging time at an isothermal aging process is given in the following way. The real and imaginary parts of the complex electric capacitance are given as:

$$C'(\omega, T, t) = (\epsilon_\infty(T, t) + \epsilon'_{\text{disp}}(\omega, T, t))C_0(T, t) \quad (3.1)$$

$$C''(\omega, T, t) = \epsilon''_{\text{disp}}(\omega, T, t)C_0(T, t), \quad (3.2)$$

where ϵ_∞ is the dielectric constant at high frequency limit, ϵ'_{disp} and ϵ''_{disp} are frequency-dependent contributions to dielectric constant due to orientational polarization associated with molecular motions. Here, there are relations as follows: $\epsilon' = \epsilon'_{\text{disp}} + \epsilon_\infty$ and $\epsilon'' = \epsilon''_{\text{disp}}$. In the case of a-PS, because the polarity is very weak, it can be expected that $\epsilon'_{\text{disp}} \ll \epsilon_\infty$. Therefore, Eq.(3.1) can be rewritten approximately as

$$C'(\omega, T, t) \approx \epsilon_\infty(T, t)C_0(T, t) \quad (3.3)$$

For an isothermal aging process, it is expected that the density increases with aging time, and hence d decreases, on condition that S remains constant. This density change, therefore, causes the increase both in ϵ_∞ and C_0 , as a result, in C' according to the discussion given in Ref. [9].

On the other hand, Eq.(3.2) shows that C'' includes two different contributions from ϵ''_{disp} and C_0 . For the isothermal aging, C_0 should increase with aging time, because the density increases, *i.e.*, the film thickness decreases, as shown in the above. If ϵ''_{disp} decreases with aging time, the contribution from ϵ''_{disp} can compete with that from C_0 , and there will be a possibility that C'' decreases with increasing aging time. For PMMA, which has a strong polar group within a chain, it has been reported that both ϵ' and ϵ'' decrease with aging time during isothermal aging process. If we assume that ϵ''_{disp} decreases with increasing aging time for a-PS in the similar way as observed in PMMA, and that the decrease in

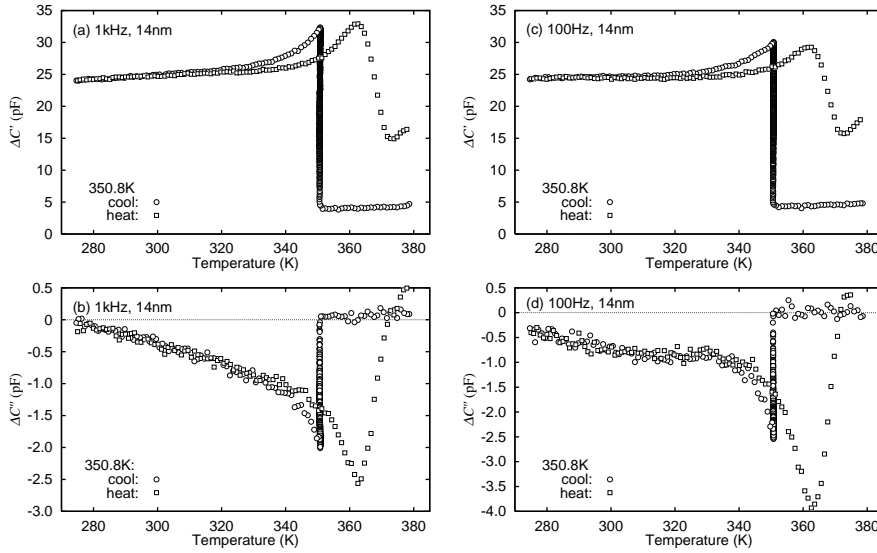


Fig. 2. Temperature dependence of the deviation $\Delta C'$ ($\Delta C''$) of the component of the complex electric capacitance C' (C'') from the reference values observed for the cooling process (circles) including at isothermal aging at 350.8K and the subsequent heating process (boxes) for thin films of a-PS with $d=14\text{nm}$ and $f=1\text{kHz}$ ((a), (b)) and 100Hz ((c), (d)).

ϵ''_{disp} overcomes the increase in C_0 , C'' can be decreased with increasing aging time. From the above discussions, the results observed in a-PS can be explained as follows: for the isothermal aging process, the decrease in d is observed as the increase in C' , while the decrease in ϵ'' is observed as the decrease in C'' . Therefore, the present measurement will give us information on the change in volume and dielectric permittivity simultaneously for the same sample during the isothermal aging process.

4 MEMORY AND 'REJUVENATION' IN THIN FILMS

Fig.2 shows temperature dependence of $\Delta C'$ and $\Delta C''$ observed during the cooling process including isothermal aging at T_a and the subsequent heating process for $f=1\text{kHz}$ and 100Hz . In this case, $\Delta C'(T)$ ($\Delta C''(T)$) are evaluated as the deviation of $C'(T)$ ($C''(T)$) from reference values $C'_{\text{ref}}(T)$ ($C''_{\text{ref}}(T)$). As the reference value of the cooling (heating) process, we used the data measured for the preceding cooling (heating) process without any isothermal aging.

Fig.2(a) shows that as the temperature decreases from 380K to 350.8K, $\Delta C'$ remains almost constant, and then $\Delta C'$ becomes larger as the aging time increases during the isothermal aging at 350.8 K. During the cooling process after the isothermal aging, the deviation becomes smaller and then approaches to a constant value, but *not to zero*. As a result, most part of the deviation $\Delta C'$ induced during the isothermal aging remains even at 273 K. This result may be associated with the fact that the isothermal aging increases the density. For the subsequent heating process, $\Delta C'$ changes along the path traced by $\Delta C'$ for the preceding cooling process after the isothermal aging, and then $\Delta C'$ shows a maximum just above T_a . After that $\Delta C'$ rapidly decreases approaching a value above zero. This behavior can be interpreted as follows: the fact that the sample experiences the aging at T_a by the way of the cooling process is memorized within the sample, and the memory is recalled during the subsequent heating process. Here, it should be noted that there are two interesting behavior. First, we find that there is a small deviation from zero between 350.8K and 380K for the cooling process. Secondly, there is an appreciable difference between $\Delta C'$ at 380K before and after the temperature cycle, in which temperature changes from 380K \rightarrow 273K \rightarrow 380K. If the sample is in an equilibrium

state above T_g , both the deviations should vanish. Furthermore, the existence of such deviations above T_g is not observed for the bulk sample ($d=293$ nm). This result implies that thin films of a-PS are not in the equilibrium state even above T_g , which may be related to the existence of a slow relaxation process of film thickness in ultra thin films [13,14].

The temperature dependence of $\Delta C''$ is different from that of $\Delta C'$, as shown in Fig.2(b). For the cooling process from 380K, $\Delta C''$ remains almost zero, and then $\Delta C''$ decreases with aging time for the isothermal aging. After that, $\Delta C''$ increases with decreasing temperature and reaches zero at about 273K, which suggests that the system is ‘*rejuvenated*’ as for the dielectric response.

Combining the results observed for $\Delta C'$ and $\Delta C''$, it is concluded that the volume of thin films of a-PS becomes smaller during the isothermal aging, and this deviation from the reference value is kept even below the aging temperature. On the other hand, dielectric permittivity also becomes smaller during the isothermal aging, and the deviation of the dielectric permittivity from the reference value is totally ‘*rejuvenated*’ at lower temperature. The existence of the volume change observed in the present measurement is consistent with the fact that there are several reports relating to the change in volume or density due to physical aging. Although the system is not rejuvenated judging only from the volume of the system, the dielectric response to electric field is fully ‘*rejuvenated*’.

Fig.2(d) shows the temperature dependence of $\Delta C''$ for the same temperature change for $f=100$ Hz. In this figure, it is found that $\Delta C''$ does not increase smoothly as the temperature changes from T_a to 273K after the isothermal aging, but there is a plateau between 330 K to 300 K for $f=100$ Hz. This plateau region can be observed only in the ultra thin films, not in the bulk sample. The position of the plateau almost coincides with that of an additional relaxation process, which can be observed only in thin films and is referred to as the α_l -process [9]. It is expected that the molecular motion corresponding to the α_l -process may be due to the segmental motion in a mobile region in thin films. In Fig.2(d), there might be a possibility that the ‘*rejuvenation*’ is suppressed by the existence of the α_l -process during the cooling process after the isothermal aging for $f=100$ Hz. It is expected that detailed investigations on the relation between the α_l -process and the rejuvenation effect will lead to understanding the mechanism of the memory and ‘*rejuvenation*’ effects in thin film geometry.

ACKNOWLEDGEMENTS

The authors appreciate K.Takegawa and Y.Saruyama for useful collaboration. This work was supported by a Grant-in-Aid for Scientific Research (B) (No. 16340122) from Japan Society for the Promotion of Science and for Exploratory Research (No. 16654068) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

References

- [1] L.C.Struick: “Physical Aging in Amorphous Polymers and Other Materials”, Elsevier, 1978.
- [2] J-P. Bouchaud, in ‘Soft and fragile matter’ edited by M.E. Cates and M.R.Evans, (IOP, 2000) p.185.
- [3] L.Bellon, S. Ciliberto, C. Laroche, Eur. Phys. J. **B25**, 223 (2002).
- [4] K.Fukao, A.Sakamoto, Y.Kubota, Y.Saruyama, J. Non-Cryst. Solids, **351** 2678 (2005).
- [5] K. Fukao, A. Sakamoto, Phys. Rev. **E71** 041803 (2005).
- [6] F.Lefloch, J.Hammann, M.Ocio, E.Vincent, Europhys. Lett. **18**, 647 (1992).
- [7] E.Vincent, J-P. Bouchaud, J.Hamman, F. Lefloch, Phil. Mag. **B71** 489 (1995).
- [8] J.L. Keddie, R.A.L. Jones, R.A. Cory, Europhys. Lett. **27**, 57 (1994).
- [9] K.Fukao and Y.Miyamoto, Phys.Rev. **E61**, 1743 (2000).
- [10] K.Fukao and Y.Miyamoto, Phys.Rev. **E64**, 011803 (2001).
- [11] A.Serghei, H.Huth, M.Schellenberger, C.Schick, F.Kremer, Phys. Rev. **E71**, 061801 (2005).
- [12] V.Lupascu, H.Huth, C.Schick, M.Wübbenhorst, Thermochemica Acta **432**, 222 (2005).
- [13] T. Kanaya *et. al.*, Polymer **44** 3769 (2003).
- [14] G. Reiter *et. al.*, Nature materials, **4** 754 (2005).